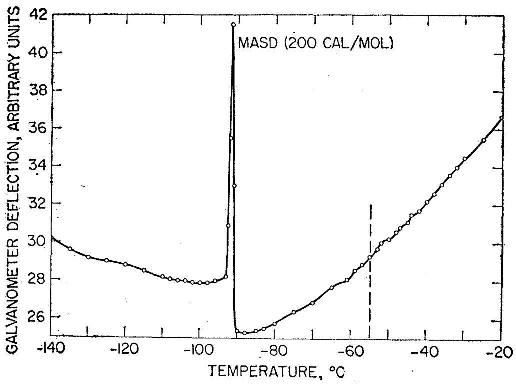

FIG. 4. Differential thermal analysis: glycine silver nitrate compared to methylammonium aluminum sulfate alum (MASD). Ordinate = galvanometer deflection, in arbitrary units. Vertical dashed line indicates temperature of dielectric anomaly of glycine silver nitrate.

Fig. 1; Fig. 2 shows the dielectric constant *vs* temperature curve; and Fig. 3 gives the variation of coercive field with temperature. The spontaneous polarization is 0.55×10^{-6} coulomb/cm^2 at 195°C. The behavior of the spontaneous polarization as a function of temperature suggests that the transition is of second order. The coercive field at −195°C is 740 v/cm, and this field drops as the Curie temperature is approached, in a manner suggestive of the behavior of triglycine sulfate.[3] No dielectric anomalies appear between −55°C and 4°K.

The result of a differential thermal analysis is shown in Fig. 4. Methylammonium aluminum sulfate alum is used as reference material. If a thermal anomaly exists in glycine silver nitrate, its magnitude is less than the experimental error.

An x-ray examination of the structure, both above and below the Curie point, is in progress.

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[3] Hoshino, Mitsui, Jona, and Pepinsky, Phys. Rev. (to be published).

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Remarks on Zener's Classical Theory of the Temperature Dependence of Magnetic Anisotropy Energy

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The temperature dependence of the first anisotropy constant for nickel is calculated by averaging the local anisotropy energy over a Langevin function. Reasonably good agreement with the experimental curve is obtained for $T/\theta>0.3$.

An estimate has been made of the variation of the local anisotropy constant with changes in volume.

ACCORDING to Zener's theory[1] the macroscopic anisotropy energy,

$$E_{\text{mag}}=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+\cdots,$$

of a cubic ferromagnetic crystal is the average of a local anisotropy,

$$e_{\text{mag}}=k_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+\cdots,$$

which for any particular magnetic spin moment results from the interaction with the orbital moments of its neighbors, the average taken over the whole distribution of spin orientations corresponding to a given temperature. Zener assumes k_1 to be constant $[k_1=K_1(0)]$ and uses for representation of spin deviations a random-walk function of the form

$$R(\theta)=\sum_{n=0}^{\infty}c_n\left(\frac{I_s(T)}{I_s(0)}\right)^{n(n+1)/2}P_n(\cos\theta),$$

which is a solution of the diffusion equation and is determined such as to give the correct average $\langle\cos\theta\rangle=I_s(T)/I_s(0)$. Thus Zener obtains

$$K_1(T)=K_1(0)\{I_s(T)/I_s(0)\}^{10},$$

a result which fits excellently to the experimental curve for iron, but fails completely in the case of nickel where one finds approximately $K_1(T)=K_1(0)\{I_s(T)/I_s(0)\}^{21}$.

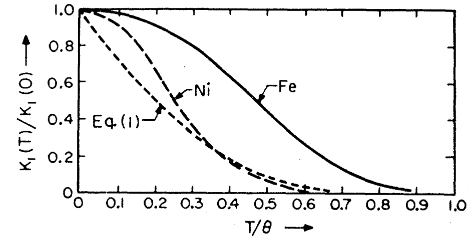

FIG. 1. Temperature dependence of anisotropy energy in Fe and Ni (experimental) and theoretical curve for Boltzmann-distributed spins [Eq. (1)].

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[1] C. Zener, Phys. Rev. **96**, 1335 (1954).

Since one cannot see any reason why the proposed model should hold for iron only, the writer supposes that the assumption $k_1=$ constant and the choice of the distribution function $R(\theta)$ should be responsible for the failure of Zener's theory in nickel.

Now, first of all one has to point out that with a constant k_1 any distribution function gives for small temperatures $K_1(T)=K_1(0)\{I_s(T)/I_s(0)\}^{10}$. For a proof of this fact, which does not need to be given here, the writer is indebted to Professor Zener. Only the random walk function, however, seems to yield the tenth power of $I_s(T)/I_s(0)$ for all temperatures up to the Curie point. If instead of the random walk function one inserts the conventional Boltzmann distribution

$$f(\theta)=c\exp\left\{\frac{\alpha I_s(T)}{kT}\cos\theta\right\}\sin\theta,$$

one obtains

$$K_1(T)/K_1(0)=1-\frac{10}{3}\frac{T}{\theta}+\frac{35}{9}\left(1-\frac{T}{\theta}\right)\left(\frac{T}{\theta}\right)^2 \times\left(\frac{I_s(0)}{I_s(T)}\right)^2 \qquad (1)$$

(Fig. 1), where θ is the Curie temperature and where, according to the Langevin-Weiss formula,

$$\frac{I_s(T)}{I_s(0)}=\coth\left(\frac{3\theta}{T}\frac{I_s(T)}{I_s(0)}\right)-\frac{T}{3\theta}\frac{I_s(0)}{I_s(T)}. \qquad (2)$$

Equation (1) decreases at small T/θ's also like $\{I_s(T)/I_s(0)\}^{10}$, but becomes steeper at elevated temperatures and fits well to the experimental nickel curve for $T/\theta>0.3$. If one inserts in Eq. (1) experimental values of $I_s(T)/I_s(0)$, one obtains yet smaller values of $K_1(T)/K_1(0)$. Altogether this shows that the result of treating the Zener model depends decisively on the choice of the spin distribution function.

Rebus sic stantibus, it seems desirable now to try quantum-statistical spin distributions which, as is well known, yield much better temperature curves of saturation magnetization than classical distributions like Eq. (2). But such an attempt encounters considerable difficulties. One obtains the best I_s *vs* T curves for $j=\frac{1}{2}$, i.e., one Bohr magneton per atom. Since in this case there are only two spin orientations, one parallel to the direction of spontaneous magnetization and one antiparallel, Zener's model gives no temperature dependence of anisotropy energy at all, because e_{mag} is equal for both orientations. This seems to indicate that quantum-statistical distributions are not adequate for a treatment of our model. This does not necessarily contradict the fundamental concepts of the model. The fact that just the case $j=\frac{1}{2}$ gives the best saturation curves for nickel and iron, though neither in nickel nor in iron is the number of Bohr magnetons per atom one, but rather 0.6 and 2.2, respectively, makes the assumption of discontinuous distributions of spin orientation doubtful in general. The assumption that an atomic magnetic moment in a field can assume only a limited number of orientations with respect to the direction of the field, holds rigorously only for free atomic moments, for example those of gas molecules. In analogy to the electronic energy levels, however, which broaden when atoms are brought together to form a crystal lattice, it should be possible that the orientation ranges of the atomic magnetic moments broaden too as a consequence of exchange and spin-orbit coupling with the neighbors. They may even form a quasi-continuum. The often successful application of Dirac's exchange-energy expression,

$$E_A=A\sum_{i,k}(\mathbf{s}_i\cdot\mathbf{s}_k), \qquad (3)$$

e.g., in the theory of domain walls, emphasizes the assumption that—more than is hitherto usual—Eq. (3) may be considered not only as an operator but in a sufficient approximation as the real value of the exchange interaction energy for any angle between $\mathbf{s}_i$ and $\mathbf{s}_k$. Then one has a lattice of magnetic spin moments which are coupled to one another by a sort of elastic binding and perform oscillations at raised temperature. This gives a picture of spin waves, not in the somehow abstract sense hitherto convenient, but spin waves as wavelike deviations of spin orientation. A "Debye theory" of these spin lattice oscillations with all its consequences (e.g., a zero-point oscillation at $T=0$) has not yet been developed.

Such a theory may reveal structure-dependent differences between the spin distributions of body-centered iron and face-centered nickel and thus within the framework of Zener's model may explain partially the differences in the temperature dependences of anisotropy energy. However, in addition, we should abandon the assumption $k_1=$ const, and consider a different temperature dependence of k_1 in Fe and Ni. A temperature dependence of k_1 is necessary from the following reasons:

(1) k_1 must depend on temperature since spin-orbit interaction varies with increasing intensity of atomic vibrations.

(2) In a number of metals and alloys (for example nickel) K_1 changes its sign. The average of $k_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)$, however, has the same sign as k_1 has. If one sets $k_1=K_1(0)$ a change of sign is not possible.

(3) Magnetic anisotropy energy varies with increasing temperature also in consequence of lattice dilatation. During an isotropic dilatation of a cubic crystal,[2] $e_{ik}=(\Delta V/3V_0)\delta_{ik}$ (where δ_{ik} is the Kronecker symbol), K_1 varies as

$$\Delta K_1=b_3(\Delta V/V_0),$$

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[2] R. Becker and W. Döring, *Ferromagnetismus* (Verlag Julius Springer, Berlin, 1939), pp. 136, 298.

where b_3 is the third magnetoelastic constant.[2] If $\alpha=(dV/dT)/V_0$ is the volume expansion coefficient, we thus obtain for the thermal isotropic dilatation an additional temperature dependence of K_1:

$$\delta K_1 = b_3 \alpha \delta T.$$

The constant b_3 may be obtained from measurements of volume magnetostriction, but this procedure is difficult and the uncertainties are often as large as b_3 itself. Becker and Döring[2] give on page 298, for room temperature,

$$\begin{aligned} b_3 &= 5.2\times 10^6\ \text{erg/cm}^3 \quad \text{for Fe,} \\ b_3 &= -1.2\times 10^6\ \text{erg/cm}^3 \quad \text{for Ni.} \end{aligned} \tag{4}$$

It is very remarkable that the volume effect thus increases magnetic anisotropy (lattice dilatation makes K_1 more positive for iron, more negative for nickel). Since all anisotropy effects must decrease with infinitely increasing distance of the atoms, b_3 should in both cases go through zero somewhere above room temperature (maybe above the Curie point).

With (4) and $\alpha_{\text{Fe}}=3.5\times 10^{-5}/°\text{K}$, $\alpha_{\text{Ni}}=4\times 10^{-5}/°\text{K}$, one obtains

$$dK_1/dT = 182\ \text{erg/cm}^3\ °\text{K}, \qquad \text{(Fe)}$$

$$dK_1/dT = -48\ \text{erg/cm}^3\ °\text{K}, \qquad \text{(Ni)}$$

as compared with the experimental values

$$dK_1/dT \approx -750\ \text{erg/cm}^3\ °\text{K}, \qquad \text{(Fe)}$$

$$dK_1/dT \approx 1000\ \text{erg/cm}^3\ °\text{K}. \qquad \text{(Ni)}$$

The contribution of vacuum expansion to dK_1/dT at room temperature is therefore not negligible.

As Dr. W. J. Carr has recently pointed out to the writer, the volume effect on K_1 appears to result from a volume dependence of k_1 as well as of the exchange integral and therefore of the saturation magnetization.[3] These two effects may not be separated by inspection of experimental data. In Zener's theory the volume dependence of the exchange energy may perhaps be accounted for by inserting the experimental $I_s(T)$ as parameter.

If we write

$$K_1(T) = k_1\{I_s(T)/I_s(0)\}^n$$

(where $n=10$ for iron, $n=21$ for nickel), k_1 is in both cases approximately a constant according to experiment. If, however, we give k_1 the meaning that it has in Zener's model, it must depend on volume. This may be shown in the following way:

$$\frac{b_3}{K_1} = \frac{V_0}{K_1}\frac{dK_1}{dV} = V_0\left\{\frac{d\ln|k_1|}{dV} + \frac{n}{I_s}\frac{dI_s}{dV}\right\}$$

can be brought into the form[4]

$$\frac{b_3}{K_1} = \frac{d\ln|k_1|}{dV/V_0} + n\frac{K}{I_s}\left(\frac{\partial V/V_0}{\partial H}\right)_{\text{saturation}},$$

where K is the bulk modulus. $\partial(V/V_0)/\partial H$ was found by Snoek[5] to be $(5\text{—}5.3)\times 10^{-10}$ and 0.95×10^{-10} for iron and nickel, respectively (at room temperature).

Thus we obtain

$$\begin{aligned} 9.6 &= d\ln|k_1|/d(V/V_0) + 5.3 \quad \text{(Fe),} \\ 2.1 &= d\ln|k_1|/d(V/V_0) + 3.7 \quad \text{(Ni).} \end{aligned} \tag{5}$$

This should provide experimental evidence for the temperature variance of k_1. In a rather heuristic manner we may furthermore conclude from (5) that $|k_1|$ increases with increasing temperature in Fe and decreases in Ni.

As long as more is not known about the temperature variation of b_3, it is uncertain whether the differences between the temperature dependences of K_1(Fe) and K_1(Ni) may entirely be interpreted by means of this volume effect. But it might be possible that the temperature variation of the spin distribution (the exchange integral assumed to be constant) yields a ratio $K_1(T)/K_1(0)$ which (except for very small temperatures) decreases a little faster than $\{I_s(T)/I_s(0)\}^{21}$, and that the comparatively small volume effect in nickel results in $K_1(T)/K_1(0) \approx \{I_s(T)/I_s(0)\}^{21}$, the large volume effect in iron, however, in $K_1(T)/K_1(0) \approx \{I_s(T)/I_s(0)\}^{10}$.

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[3] W. J. Carr (private communication).

[4] W. J. Carr, reference 3. See also Becker and Döring, reference 2, p. 299.

[5] J. L. Snoek, Physica 4, 853 (1937).